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DESENSITIZATION OF ZIRCONIUM POWDER USED IN PRIMERS

Phase IV - Final Report

by

GEORGE NORWITZ  
JOHN J. JACKIEWICZ

December 1966

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**QUALITY ASSURANCE DIRECTORATE  
FRANKFORD ARSENAL  
Philadelphia, Pa. 19137**

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## I. SUMMARY

The mechanics of the desensitization process for zirconium powder used in primers wherein zirconium powder is treated with 1% hydrofluoric acid is considered. On the basis of experimental work and logical deduction it is concluded that the process consists of the dissolution of the oxide surface and the formation of a layer of zirconium hydride containing some fluoride. A method was developed for the determination of the fluoride colorimetrically by the zirconium-alizarin colorimetric method after prior dissolution of the coating by digestion with hot 10% sodium hydroxide solution. The only significant difference between treated and untreated samples was the hydrogen and fluoride contents. Treated zirconium had a hydrogen content that averaged 0.035% higher than untreated powders. Treated zirconium contained about 0.14% fluoride. Various other aspects of the coating were considered. The desensitization process is useful to Ordnance, particularly if the zirconium powder in question is overly sensitive (that is, if it does not pass the electrostatic energy test). The effect of impurities on the sensitivity of zirconium powders is discussed.

## II. RECOMMENDATIONS

The following recommendations are made:

1. The hydrofluoric acid desensitization process should be used to desensitize zirconium powder that is overly sensitive (zirconium powder used in primers is considered overly sensitive when it is ignited by the application of electrostatic energy of less than 0.04 joule).
2. The permissible limits of impurities in zirconium powder as well as the quality assurance provisions in Military Specification MIL-Z-399C, Zirconium (Granular and Powdered), July 1965 (proposed) be revised.

## III. INTRODUCTION

Zirconium powder is an important commodity and much effort has been devoted to desensitization processes that would make it less sensitive to premature ignition.

The following desensitization procedures have been proposed, some quite recently: coating with copper by a displacement method that was not specified (11), coating with nickel by use of a solution of nickel chloride, sodium acetate, and hydrofluoric acid (7), coating with plastic by use of a solution of nylon (Zytel 63), polyvinyl alcohol, or Viton A in acetone (24), coating with plastic by use of a solution of polystyrene in benzene (15), coating with a surface active agent (Alkaterge-T) (24), coating with mineral oil as recommended by Allegheny Ballistics Laboratory (24), and treatment with 1% hydrofluoric acid (13, 14).

The hydrofluoric acid method consists essentially of treating zirconium powder with 1% hydrofluoric acid for 5 minutes, then adding ice water to stop the reaction, filtering, and washing with water, acetone, and ether (13) (14). It was believed that the reason for the effectiveness of the technique was the formation of a coating of zirconium hydride, a material that is known to be much less sensitive to ignition than is zirconium metal (14). The reason for the deduction that a coating of zirconium hydride was produced by the method is due to the fact that previous investigators have found by means of X-ray diffraction that zirconium hydride was produced on pieces of zirconium metal on treatment that dilute hydrofluoric acid (12, 16, 28). Later chemical work described in a laboratory report (21) showed that the hydrogen content of zirconium powder increased on the average about 0.035% after being desensitized.

The purpose of the present report was to investigate further the mechanism of the desensitization process. Another purpose was to present the findings of this laboratory on what makes zirconium powder overly sensitive. If the zirconium powder is not too sensitive, the application of a desensitization process is, of course, unnecessary.

#### IV. STUDY

##### A. DEVELOPMENT OF METHOD FOR THE DETERMINATION OF FLUORIDE IN THE COATING

The accurate determination of small amounts of fluoride in the presence of large amounts of zirconium is a difficult analytical problem. Formerly, a problem existed for the determination of fluoride in zirconium metal itself because one method for producing zirconium powder was to react zirconium tetrafluoride with calcium, magnesium, or sodium. These processes are now considered obsolete (6, 29) (principally because of the low volatility of the alkaline earth and alkaline metal fluorides and their toxicity). Patent applications have been issued for the production of zirconium metal by the electrolysis of molten mixtures of zirconium fluoride and other salts, but apparently these proposed electrolytic methods have not

progressed beyond the pilot plant stage. This laboratory has not encountered zirconium powder produced by a fluoride process.

In 1950 in connection with experimental work on the production of zirconium by use of fluoride processes, a method was proposed for the determination of fluoride in zirconium by igniting the zirconium in a platinum tube with a stream of moist oxygen and titrating the resultant hydrogen fluoride with thorium nitrate, using sodium alizarin sulfonate indicator (9). This method was an extension of the pyrohydrolysis technique that had been used for the determination of the fluoride content of fluoride salts (for example, zirconium fluoride) (23, 30). Lewis, Nardozzi, and Melnick (17) in applying the pyrohydrolysis technique to the determination of fluoride in slags observed that incomplete recovery was obtained even after ignition for 2 hours. They found that complete recovery of fluoride could only be obtained by mixing the slag with tungstic oxide (which acts as an accelerator (23)) prior to the ignition. No experiments were conducted with the pyrohydrolytic technique since it is somewhat troublesome.

Some experiments were conducted on the dissolution of the entire sample in order to determine the fluoride content of the coating. In some of these experiments the sample was dissolved by heating with sulfuric acid in a distillation apparatus and at the same time collecting the distilled sulfuric acid under alkali. Presumably, the fluoride would distill over as a mixture of hydrofluoric acid, silicon fluoride, and fluosilicic acid. Very low results for fluoride were obtained by this method (colorimetrically after redistillation as fluosilicic acid to remove sulfate). Better recoveries might possibly have been obtained by fuming twice with intervening additions of water. However, the method of attack was not pursued further because it was cumbersome. It is to be noted that zirconium in solution seems to repress the distillation of fluoride.

Dissolution of the entire sample by fusion with sodium carbonate, addition of water, filtration of the precipitated zirconium carbonate, and analysis of the filtrate for fluoride gave very low results, presumably because of coprecipitation of the fluoride with the zirconium carbonate.

Since methods for the determination of the fluoride in the coating by dissolution of the entire sample were unsuccessful, attention was turned to dissolution of the coating alone. It was found that this could be usually done with fair success by boiling with 30% sulfuric acid at 135° C. in a distillation flask and then steam distilling the fluoride as fluosilicic acid in the usual manner (1, 10) (glass beads and the flasks furnish the source of the silica). Since the samples lost 10% of their weight by this treatment, it could be assumed that the coating was completely dissolved. This method was subsequently abandoned because erratic results were frequently obtained.

The best method found for analyzing the coating was to treat the zirconium powder with hot 10% sodium hydroxide solution, filter, and determine the fluoride in the filtrate (colorimetrically by the zirconium-alizarin color (2, 19). In the final recommended treatment a 0.2-gram sample was boiled with 10 ml of the sodium hydroxide solution for 1/2 minute and the heating continued at 80° to 90° C. for 10 minutes. This treatment removed the fluoride coating, since no fluoride could be recovered on further treatment.

After the filtration, it was necessary to adjust the acidity, prior to the colorimetric determination. This could only be done by use of nitric acid, since other acids interfered with the color. The adjustment was made by adding phenolphthalein indicator and adding nitric acid (1 to 1) until the indicator became colorless. An investigation of the effect of nitric acid (Table I) showed that no more than 1 to 3 drops excess of nitric acid (1 to 1) should be present. A larger excess caused the color to decrease in intensity.

Ordinarily, it is recommended that in the colorimetric determination of fluoride by the zirconium-alizarin complex that the transmittance be measured in  $60 \pm 5$  minutes (2, 19). A study of the effect of time on the development of the color by the proposed procedure (Table II) showed that 1-1/2 hours was required for full development (probably because of the influence of the nitrate) and that the color then remained constant for an additional half hour. It then increased in intensity somewhat on standing overnight. It is recommended that the transmittance be measured in 1-1/2 to 2 hours.

The calibration curve was prepared by adding standard sodium fluoride solution to portions of untreated zirconium and carrying the samples through the procedure. This technique compensated for the slight amount of zirconium that was dissolved by the sodium hydroxide solution. The dissolved zirconium affected the color somewhat because the intensity of the zirconium-alizarin complex depends to some extent on the amount of zirconium present.

#### B. RECOMMENDED METHOD FOR THE DETERMINATION OF FLUORIDE

##### Reagents

Standard sodium fluoride solution (1 ml = 0.1 mg of F). Dissolve 0.2210 gram of reagent grade sodium fluoride in water and dilute to 1 liter in a volumetric flask.

Sodium hydroxide solution (10%). Dissolve 100 grams of reagent grade sodium hydroxide pellets in water and dilute to 1 liter.



Phenolphthalein indicator solution (0.1%). Dissolve 0.1 gram of phenolphthalein in 100 ml of 95% ethyl alcohol.

Alizarin red S solution. Dissolve 0.75 gram of alizarin red S in 900 ml of water, filter (if not clear), and dilute to 1 liter. Protect from direct sunlight.

Acid zirconium solution. Dissolve 0.294 gram of reagent grade  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (or 0.354 gram of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) in about 700 ml of water. Add 33 ml of sulfuric acid and 100 ml of hydrochloric acid while stirring. Cool to room temperature and dilute to 1 liter. After 1 hour the reagent is ready for use.

#### Preparation of Calibration Curve

Transfer six 0.2-gram samples of untreated zirconium powder to 250-ml beakers and add 2.0, 2.5, 3.0, 3.5, and 4-ml portions of standard sodium fluoride solution. Use one sample as a blank. Add 10 ml of sodium hydroxide solution (10%) and cover with watch glasses. Boil for 1/2 minute and then digest at 80° to 90° C. for 10 minutes, swirling occasionally. Add 30 ml of water, filter through Whatman No. 41H filter paper and wash with water. Add 2 drops of phenolphthalein indicator solution, then add nitric acid (1 to 1) from a buret until the pink color just disappears. Cool to 20° C. and add 5.00 ml of alizarin red S solution (this may cause the color of the indicator to change momentarily) and 5.00 ml of acid zirconium solution. Wash into 100-ml volumetric flasks and dilute to the mark. Let stand 1-1/2 to 2 hours and determine the transmittance at 535 millimicrons by a spectrophotometer that has been set to 100 per cent transmittance with the reagent blank. Plot milligrams of fluoride against per cent transmittance.

Prepare a new calibration curve with every lot of reagents.

#### Procedure

Weigh a 0.2-gram sample into a 250-ml beaker and also weigh 0.2 gram of untreated zirconium powder for a blank. Proceed as above. Convert the reading to milligrams of fluoride by consulting the calibration curve. Calculate as follows:

$$\% \text{ F} = \frac{\text{mg of F as read from curve}}{\text{grams sample} \times 10}$$

### C. RESULTS FOR FLUORIDE

The results obtained for three samples of treated zirconium powder are shown in Table III. The average amount of fluoride in these samples was 0.14%. No fluoride was found in the untreated samples.

### D. MECHANICS OF THE DESENSITIZATION PROCESS

The average chemical results for the analysis of treated and untreated zirconium powders (excluding the fluoride content which was reported above) are summarized in Table IV. Results are given for the following elements: hydrogen, carbon, oxygen, iron, nitrogen, silicon, chloride, titanium, manganese, nickel, chromium, molybdenum, tungsten, vanadium, phosphorus, cobalt, copper, and aluminum. The hydrogen and carbon were run by combustion and the oxygen by bromination (21). The remaining elements were run by standard methods (22).

It is seen that as a result of the desensitization treatment the hydrogen content increased on the average by about 0.035% but that the other elements did not change significantly, although there was a slight decrease in the silicon content.

The fact that the elements did not change significantly would indicate that the desensitization process could not merely be the dissolution of impurities. Also, if this were the explanation of desensitization then a hydrofluoric - nitric acid solution would work as well as the hydrofluoric acid solution. In actuality, a hydrofluoric - nitric acid solution is ineffective since the nitric acid prevents the generation of hydrogen.

Although dissolution of impurities is not the explanation of desensitization it is true that the thin oxide coating would be dissolved prior to the deposition of the zirconium hydride coating.

As stated previously (14) the particle size is not significantly changed by the desensitization treatment. It should be pointed out, however, that the Andreassen pipet method used characterized the smallest particles as 10 microns or less. It would seem that particles in the range of 1 micron would be dissolved completely by the process. The dissolution of micro particles could not be the explanation of desensitization; if it were, a hydrofluoric - nitric acid solution would also be effective.

As shown by microphotographs (14) the particle shape and protuberances are not changed significantly, therefore, change in physical configuration has no bearing in desensitization.

Attempts to study the coating by X-ray diffraction failed because of interference by zirconium. Previous investigators studied the zirconium hydride coating on pieces of zirconium after first removing the coating mechanically by rubbing with a rubber squeegee, a technique obviously not applicable to zirconium powder.

Judging by the work of Bomberger and Knopek (8) on titanium hydride coating obtained by treating sheets of titanium with 4% hydrofluoric acid solution, it would be expected that the formula of zirconium hydride in the coating would be  $ZrH_2$ . Bomberger and Knopek dissolved away measured thicknesses of the titanium hydride coating on titanium sheets with a mixture of hydrofluoric and nitric acids and determined the hydrogen content of the sample after each dissolution. They found that the hydrogen content decreased with the depth but that there was very little hydrogen at a depth greater than 0.001 inch. They concluded that the formula of the coating of titanium hydride approached the formula  $TiH_2$ .

As stated previously, the hydrogen content of the treated zirconium increased on the average about 0.035% as a result of the desensitization treatment. On the assumption that two atoms of hydrogen is equivalent to 1 molecule of  $ZrH_2$ , it can be deduced that there should be about 1.6% zirconium hydride present.

It should be pointed out, however, that  $ZrH_2$  is not a saline-type hydride nor an actual chemical compound but an interstitial solid solution (in reality the amount of hydrogen is somewhat less than represented by the formula  $ZrH_2$ ; the true formula is probably  $ZrH_{1.96}$ ). Several phases of the zirconium-hydrogen system have been identified ranging in composition from  $ZrH_{1.54}$  to  $ZrH_{1.96}$  (5).

The density of pure zirconium metal is 6.40 whereas the density of  $ZrH_{1.96}$  is 5.47. It would seem, therefore, that the expansion in volume when zirconium is converted to zirconium hydride would make for a porous coating. This does not occur, however, since in going from zirconium metal to zirconium hydride the metal lattice rearranges into a new structure and thus relieves strains set up during expansion. Zirconium has a hexagonal structure while  $ZrH_{1.96}$  has a tetragonal structure (5). The structure is determined by the use of X-rays.

The fluoride in the coating is tightly bound since it could not be removed by washing with dilute hydrochloric acid (1 to 5). It is probably attached to the zirconium atom in a unique way. It is doubtful that it is present as zirconium tetrafluoride or hydrofluozirconic acid since these substances are salt-like. Calculating the 0.14% fluoride as zirconium tetrafluoride would mean that there would be 0.3% zirconium tetrafluoride present, so in any case zirconium hydride is the predominant component of the coating. The fluoride, however, may play a role in the effectiveness of the coating. The reason for this belief is that the desensitization produced on treating zirconium powder with 1% sulfuric acid (30 minute treatment) is not as great as that produced by 1% hydrofluoric acid (5 minute treatment). Hydrofluoric and sulfuric acids are the only acids that attack zirconium to a significant extent.

In the formation of the coating there is continued dissolution of the zirconium and formation of the coating at the same time. The dissolution of the zirconium must take place through the pores of the coating but as the coating increases the pores become smaller. The 1% hydrofluoric acid solution is effective because it is moderate in its attack. If too strong an acid concentration is used, no significant hydride layer builds up because the dissolution rate exceeds the hydrogen diffusion rate.

The coating of zirconium hydride is continuous and stress-free. There is no contradiction between the theory of the formation of a zirconium hydride coating and the theory that premature ignition and explosion of zirconium powder is caused by hydrogen (10, 25, 27). According to the latter theory hydrogen accumulates at the grain boundaries of the zirconium powder as a lower hydride of zirconium in a stressed condition resulting from the reaction between zirconium and moisture or water that takes place under conditions that are not entirely clear. The stress continues to build up until it triggers the release of energy causing a violent reaction. This triggering action occurs especially on the application of a small outside force.

Zirconium hydride has much higher thermal and electrical conductivity than zirconium metal (5). This might be the key point in explaining why zirconium hydride and zirconium powders coated with zirconium hydride are less sensitive than zirconium. The greater thermal conductivity would mean that heat would be conducted away before it accumulates; the greater electrical conductivity would mean that the zirconium is less susceptible to ignition by electrical discharge.

#### E. EFFECT OF COMPOSITION ON THE SENSITIVITY OF ZIRCONIUM POWDER

The question is raised as to what causes a zirconium powder to be too sensitive. The question is important as far as desensitization is concerned since desensitization may not be necessary if the powder is not too sensitive.

The sensitivity of zirconium powder as measured by the electrostatic energy test is primarily dependent on particle size and composition.

Much consideration has been given by previous investigators on the effect of oxygen content on zirconium powder, but as previously summarized (14) some investigators believe that a high oxygen content increases the sensitivity, others that it decreases sensitivity, and others that it has no effect.

When zirconium is combined with hydrogen the sensitivity does not change until the composition approaches  $ZrH_2$ , at which point the sensitivity decreases considerably (4).

Powders containing several percent of copper, titanium, nickel, iron and cobalt are quite sensitive (4). It has been stated that zirconium alloys containing lead (1), chromium, titanium, and manganese (25) are pyrophoric. Zirconium alloys containing large percentages of titanium, manganese, lead, antimony, and tin have been patented for their pyrophoric properties (26). It has been claimed that moderate amounts of iron, calcium, and chloride increase the sensitivity (25).

This installation has over the past several years observed the correlation between the composition of zirconium powders and sensitivity as determined by the electrostatic energy test (ignition on the application of an electrical discharge of less than 0.04 joule). Typical chemical analyses of overly sensitive zirconium powders are the untreated samples in Table IV. These powders are not only overly sensitive but they do not function in a satisfactory manner in primers (unless they are desensitized). Other unsatisfactory zirconium powders (for primers) are shown in Table V. Typical chemical analyses of zirconium powders that passed the electrostatic energy test are shown in Table VI.

To summarize our experiences, oxygen and hydrogen content will not make the zirconium powder overly sensitive. More than small amounts of chloride, carbon, nitrogen, aluminum, calcium, iron, and molybdenum will increase the sensitivity. Up to 2% tin does not affect the sensitivity (probably because this range of tin forms a solid solution with zirconium producing corrosion-resistant zircaloy). The amount of hafnium found in zirconium does not increase the sensitivity. Hafnium is the sister element

of zirconium and is usually found associated with it in amounts of up to 1 to 2%. High purity zirconium produced for reactor purposes contains less than 0.01% hafnium. Hafnium is totaled with zirconium in ordinary methods of analysis.

There are three processes presently used in the manufacture of zirconium powder. There are: (a) heating powdered zirconium oxide with calcium, (b) heating zirconium tetrachloride with calcium (or magnesium, or sodium), followed by grinding of the resultant zirconium, and (c) heating zirconium metal with hydrogen to form zirconium hydride which is then ground and heated in a vacuum to remove the hydrogen. Obviously, the impurities present in zirconium powder will vary depending upon the raw materials and process used in the manufacture of the zirconium powder. A high nitrogen content in the zirconium powder frequently results from the high nitrogen content of calcium used as a reactant (3). Molybdenum can be introduced from molybdenum bombs (18). Oxygen or nitrogen can be picked up from the atmosphere, even though the operations are carried out under an inert gas such as helium or argon.

The present chemical requirements for zirconium powder, as cited in Military Specification MIL-Z-399C (20), are shown in Table VII. In view of the effect of impurities, it is suggested that these requirements be changed to those shown in Table VIII.

The option should be given in Military Specification MIL-Z-399C for determining the metallic impurities spectrographically (if the impurities are within the cited limits).

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#### Acknowledgment

The authors are indebted to Samuel Sitelman for his suggestions.



## VI. TABLES

Table I. Effect of Excess Nitric Acid on the Color

Excess Ml of HNO <sub>3</sub> (1 to 1) After Neutralization to Phenolphthalein	% Transmittance <sup>a</sup>
0	78
0.1	78
0.2	79
0.5	80
0.8	87
1.0	88
Blank	52

<sup>a</sup> Spectrophotometer set to 100 per cent transmittance with water.

Table II. Effect of Time on Development of Color

Mg of Fluoride	Per Cent Transmittance After				
	1 hr.	1-1/2 hrs.	2 hrs.	3 hrs.	Overnight
0.0	49	48	48	48	52
0.1	64	62	62	60	62
0.2	76	72	72	70	80
0.3	86	85	85	83	83
0.4	95	95	95	95	97

Table III. Results for Fluoride in Desensitized Zirconium Powders

<u>Sample</u>	<u>% Fluoride Found</u>
A	0.13
A	0.14
A	0.16
	Avg. 0.14
B	0.15
B	0.15
B	0.19
	Avg. 0.16
C	0.11
C	0.12
C	0.11
	Avg. 0.11

Table IV. Analysis of Untreated and Treated Zirconium Powders (%)

Sample	Electrostatic Energy (Joule)	H	C	O	Fe	N	Si	Cl	Ti	Mn	Ni
A-Untreated	0.000125	0.054	0.161	0.82	0.44	0.03	0.22	0.029	0.06	0.008	0.004
A-Treated	0.09	0.092	0.168	0.82	0.43	0.03	0.18	0.030	0.06	0.004	0.004
B-Untreated	0.00125	0.057	0.137	0.88	0.35	0.08	0.14	0.036	0.06	0.004	0.001
B-Treated	0.125	0.087	0.136	0.91	0.37	0.10	0.12	0.027	0.07	0.004	0.001
C-Untreated	<0.04	0.076	0.192	0.77	1.00	0.52	0.08	0.023	0.06	---	---
C-Treated	>0.04	0.108	0.195	0.76	1.00	0.45	0.07	0.024	0.06	---	---
D-Untreated	<0.04	0.091	0.461	1.84	0.58	0.91	0.25	0.053	0.07	0.004	0.012
D-Treated	>0.04	0.131	0.470	1.70	0.58	0.87	0.21	0.047	0.07	---	0.012
Sample		Cr	Mo	W	V	P	Co	Cu	Al <sup>a</sup>		
A-Untreated		0.002	0.21	0.006	0.004	0.015	0.0003	0.004	0.5		
A-Treated		0.002	0.24	0.008	0.002	0.015	---	0.005	0.5		
B-Untreated		0.002	0.26	0.012	0.002	0.009	0.0002	0.006	0.2		
B-Treated		0.001	0.28	0.012	0.002	0.008	0.0002	---	0.2		
C-Untreated		---	0.31	0.010	0.003	0.009	0.0000	0.005	0.2		
C-Treated		---	0.33	---	---	---	---	---	0.2		
D-Untreated		0.001	0.28	0.006	0.002	0.006	---	0.003	0.2		
D-Treated		---	0.24	0.008	---	---	---	---	0.2		

<sup>a</sup> Spectrographic

< - less than

> - more than

Table V. Analysis of Typical Unsatisfactory Zirconium Powders (%)

Sample	<u>H</u>	<u>C</u>	<u>O</u>	<u>Fe</u>	<u>N</u>	<u>Si</u>	<u>Cl</u>	<u>Ti</u>	<u>Mn</u>	<u>Ni</u>
E	0.093	0.55	1.50	0.2a	1.03	0.2a	0.10	0.00	<0.01a	0.00a
F	0.077	0.29	0.66	0.2a	0.74	0.2a	0.11	0.00	<0.01a	0.00a
G	0.034	0.30	0.72	0.2a	0.81	0.2a	0.12	0.00	<0.01a	0.00a
	<u>Cr</u>	<u>Mo</u>	<u>W</u>	<u>V</u>	<u>Co</u>	<u>Cu</u>	<u>Al</u>	<u>Sn</u>		
E	0.00a	<0.1a	0.00a	0.00a	0.00a	0.00a	<0.1a	0.00a		
F	0.00a	<0.1a	0.00a	0.00a	0.00a	0.00a	<0.1a	0.00a		
G	0.00a	<0.1a	0.00a	0.00a	0.00a	0.00a	<0.1a	0.00a		

<sup>a</sup> Spectrographic  
< - less than

Table VI. Analysis of Typical Satisfactory Zirconium Powders (%)

Sample	<u>H</u>	<u>C</u>	<u>O</u>	<u>Fe</u>	<u>N</u>	<u>Si</u>	<u>Cl</u>	<u>Ti</u>	<u>Mn</u>	<u>Ni</u>
H	0.010	0.29	0.67	0.01	0.07	0.00	0.019	0.01	0.004	0.011
I	0.051	0.030	1.09	0.11	0.04	0.01	0.016	0.04	0.004	0.011
J	0.46	0.131	1.43	0.26	0.04	0.00	0.017	0.005	0.008	0.003
	<u>Cr</u>	<u>Mo</u>	<u>W</u>	<u>V</u>	<u>P</u>	<u>Co</u>	<u>Cu</u>	<u>Al<sup>a</sup></u>	<u>Sn<sup>a</sup></u>	
H	0.001	0.000	0.002	0.001	0.000	0.0000	0.004	<0.05	0.50	
I	0.008	0.003	0.000	0.011	0.000	0.0002	0.006	<0.05	0.00	
J	0.002	0.004	0.006	0.001	0.000	0.0000	0.007	<0.05	0.00	

<sup>a</sup> Spectrographic  
<- less than

Table VII. Present Chemical Requirements for Zirconium Powder (20)

	<u>Type I</u>	<u>Type II</u>	
		<u>Grade A</u>	<u>Grade B</u>
Total zirconium (min.)	96.0%	95.0%	94.0%
Acid soluble calcium (max.)	0.05	0.05	0.10
Iron (max.)	0.30	0.03	0.20
Aluminum (max.)	0.10	0.16	0.30
Hydrogen (max.)	0.15	0.17	0.20
Chlorides (as $\text{NH}_4\text{Cl}$ ) (max.)	0.05	---	---
Silicon (max.)	0.10	---	---
Titanium (max.)	0.10	---	---
Tin (max.)	0.75	---	---

Table VIII. Recommended Chemical Requirements for Zirconium Powder

	<u>Type I</u>	<u>Type II</u>	
		<u>Grade A</u>	<u>Grade B</u>
Total zirconium (plus hafnium) (min.)	96.0%	95.0%	94.0%
Acid soluble calcium (max.)	0.05	0.05	0.10
Iron (max.)	0.30	0.03	0.20
Aluminum (max.)	0.10	0.15	0.30
Hydrogen (max.)	0.15	0.17	0.20
Chloride (as chlorine) (max.)	0.03	0.03	0.03
Silicon (max.)	0.10	0.10	0.10
Tin (max.)	0.75	0.75	0.75
Carbon (max.)	0.30	0.30	0.30
Nitrogen (max.)	0.20	0.20	0.20
Molybdenum (max.)	0.10	0.10	0.10
Other metals (max. each)	0.10	0.10	0.10

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13. ABSTRACT

The mechanics of the desensitization process for zirconium powder used in primers wherein zirconium powder is treated with 1% hydrofluoric acid is considered. On the basis of experimental work and logical deduction it is concluded that the process consists of the dissolution of the oxide surface and the formation of a layer of zirconium hydride containing some fluoride. A method was developed for the determination of the fluoride colorimetrically by the zirconium-alizarin colorimetric method after prior dissolution of the coating by digestion with hot 10% sodium hydroxide solution. The only significant difference between treated and untreated samples was the hydrogen and fluoride contents. Treated zirconium had a hydrogen content that averaged 0.035% higher than untreated powders. Treated zirconium contained about 0.14% fluoride. Various other aspects of the coating were considered. The desensitization process is useful to Ordnance particularly if the zirconium powder in question is overly sensitive (that is, if it does not pass the electrostatic energy test). The effect of impurities on the sensitivity of zirconium powders is discussed.

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